

Competing Isomeric Product Channels in the 193 nm Photodissociation of 2-Chloropropene and in the Unimolecular Dissociation of the 2-Propenyl Radical

Julie A. Mueller, Bradley F. Parsons, and Laurie J. Butler*

The James Franck Institute and Department of Chemistry,

University of Chicago, Chicago, IL 60637

Fei Qi, Osman Sorkhabi, and Arthur G. Suits

Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

Abstract

This paper presents product translational energy spectroscopy measurements of the primary photofragmentation channels of 2-chloropropene excited at 193 nm and of the unimolecular dissociation of the 2-propenyl radical. Tunable VUV photoionization of the products allows us to distinguish between the various product isomers formed in these processes. The data show evidence for three significant primary reaction channels in the dissociation of 2-chloropropene: an excited state C-Cl fission channel producing fast Cl atoms, a C-Cl fission channel producing slow Cl atoms, and HCl elimination. A minor C-CH₃ fission channel contributes as well. The measured branching of the major primary product channels is: [fast C-Cl]:[slow C-Cl]:[HCl elimination] = 62%:23%:15%. The experiments also allow us to resolve selectively the product branching between the unimolecular dissociation channels of the 2-propenyl radical, a high energy C₃H₅ isomer; we measure how the branching ratio between the two competing C-H fission channels changes as a function of the radical's internal energy. The data resolve the competition between the unimolecular H + allene and H + propyne product channels from the radical with internal energies from 0 to 18 kcal/mol above the H + propyne barrier. We find that the barrier to H + allene formation from this high energy C₃H₅ radical is higher than the barrier to H + propyne formation, in agreement with recent theoretical calculations but in sharp contrast to that predicted for the most stable C₃H₅ isomer, the allyl radical. The experiments demonstrate a general technique for selectively forming a particular C_nH_m isomer dispersed by internal energy due to the primary photolysis, thus allowing us to determine the branching between unimolecular dissociation channels as a function of the selected radical isomer's internal energy.

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* PI contact information: L. Butler, L-BUTLER@uchicago.edu, (773) 702-7206